

Cubic *Ia3d* large mesoporous silica: synthesis and replication to platinum nanowires, carbon nanorods and carbon nanotubes†

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A new synthesis route to high-quality large mesoporous cubic *Ia3d* silica is reported, utilizing a triblock copolymer (EO₂₀PO₇₀EO₂₀)–butanol mixture for the structure direction in aqueous solution.

The synthesis of cubic *Ia3d* mesoporous silica with pores larger than 5 nm has attracted much recent attention for potential applications requiring easily accessible uniform large pores. Recently, block copolymers were used to synthesize large mesoporous siliceous materials exhibiting cubic *Ia3d* symmetry.^{1–3} These syntheses were performed with a sulfur-containing silane derivative in ethanol,¹ a very high concentration of NaI salt,² or a laboratory-synthesized polymer.³ Here, we report a new synthesis route to high-quality large mesoporous cubic *Ia3d* silica, utilizing a commercially available triblock copolymer (EO₂₀PO₇₀EO₂₀)–butanol mixture for the structure direction in aqueous solution. The present method has the advantage of high reproducibility in significantly large quantities. In addition, we show that the pore shape and connectivity can be represented by a pair of interpenetrating bicontinuous networks of channels as in the structure of MCM-48,^{4,5} using a TEM imaging technique on platinum nanowires.⁶ Further, the pore diameters can be systematically tuned from 4 to 12 nm, using simple hydrothermal treatments. We show that such a high-quality, large mesoporous cubic *Ia3d* silica can be used as a template to fabricate successfully new bicontinuous arrays of nanotube-type carbon (designated as CMK-9 mesoporous carbon), as well as rod-type (CMK-8).

The large mesoporous silica with cubic *Ia3d* symmetry (designated as KIT-6) is prepared in aqueous solution using a 1 : 1 (wt%) mixture of Pluronic P123 (EO₂₀PO₇₀EO₂₀, MW = 5800, Aldrich) and butanol, around 0.5 M HCl concentrations at 25–35 °C. Either tetraethoxysilane (TEOS) or sodium silicate† is acceptable as a silica source. In a typical synthesis batch with TEOS, 6 g of P123 was dissolved in 217 g of distilled water and 11.8 g of conc. HCl (35%). To this, 6 g of butanol (Aldrich, 99.4%) was added under stirring at 35 °C. After 1 h stirring, 12.9 g of TEOS (ACROS, 98%) was added at 35 °C (TEOS : P123 : HCl : H₂O : BuOH = 1 : 0.017 : 1.83 : 195 : 1.31 in mole ratio). The mixture was left under stirring for 24 h at 35 °C, and subsequently heated for 24 h at 100 °C under static conditions in a closed polypropylene bottle (The latter is referred to as hydrothermal treatment). The solid product obtained after hydrothermal treatment was filtered and dried at 100 °C without washing. The template was removed by extraction in an ethanol–HCl mixture, followed by calcination at 550 °C. The synthesis was also carried out in a large batch (64 g of P123 with 2310 ml of H₂O). Inverse platinum replication of the mesoporous silica was performed following the method described previously.⁶ Syntheses of CMK-8 and -9 carbons followed rigorously the procedures described previously for CMK-3⁷ and CMK-5,⁸ respectively, which employed SBA-15 as the silica template.

† Electronic supplementary information (ESI) available: TEM images of mesoporous cubic silica and Pt networks, XRD patterns during formation of the cubic phase. See <http://www.rsc.org/suppdata/cc/b3/b306504a/>

The high quality of the cubic *Ia3d* silica product is judged by the powder X-ray diffraction (XRD) pattern, transmission electron microscopy (TEM) images and pore size distribution shown in Fig. 1 (see also ESI†). The material consists uniquely of large ordered domains of pure bicontinuous mesostructure. The 3-D structure is shown to be commensurate with cubic *Ia3d* symmetry, as illustrated by the images viewed along various directions. TEM images of the platinum replica obtained after dissolution of the silica template indicate large domains of 3-D Pt nanowire networks, thus revealing the interconnectivity in the pore structure of the parent cubic silica. Moreover, the Pt image shows details of self-standing branched bicontinuous systems of Pt nanowire network with different chiralities, including regular modulations in diameter. The nitrogen adsorption–desorption isotherm obtained for calcined mesoporous *Ia3d* silica (Fig. 1c) is a type IV with a sharp capillary condensation step at high relative pressures and H1 hysteresis loop, indicative of large channel-like pores in a narrow range of size. The material typically synthesized at 100 °C has a BET surface area of 800 m² g^{−1}, high pore volume reaching 1.05 cm³ g^{−1} and average pore size of 8.5 nm. Varying the hydrothermal treatment temperature between 35–130 °C allows a very effective tailoring of the mesopore diameters, ranging from 4 to 12 nm, as exemplified in Fig. 1d.

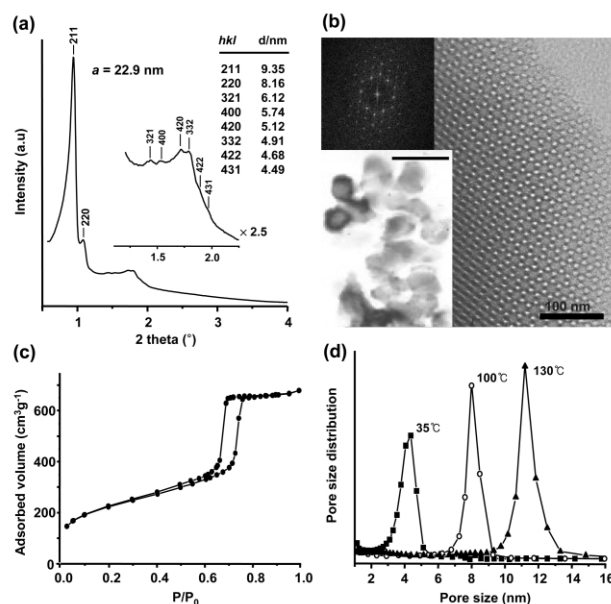


Fig. 1 a) Powder XRD patterns for calcined cubic *Ia3d* silica (KIT-6) sample templated with a P123–butanol mixture (Rigaku Multiplex, operated at 2 kW, using Cu K α radiation). b) TEM image taken along the [111] direction (Phillips F20 Tecnai, operated at 160 kV) with its Fourier diffractogram, and a TEM detail of the Pt network (scale bar is 20 nm). c) N₂ adsorption–desorption isotherm at 77 K for KIT-6 synthesized at 100 °C (Quantachrome Autosorb-1MP). d) Pore size distributions of KIT-6 synthesized at different hydrothermal treatment temperatures. The pore size was analysed using the adsorption branch using the BJH algorithm.

The present synthesis method is simple and can be used to produce large quantities of high quality cubic *Ia3d* mesoporous silica. The addition of butanol is decisive for the nature and quality of the final mesophase. At lower amounts of butanol (BuOH/P123 in weight < 0.9), a 2-D hexagonal mesophase was obtained. Furthermore, XRD results revealed that the cubic *Ia3d* phase is formed *via* a phase transformation mechanism from a lamellar phase appearing initially after 6 hours of reaction at 35 °C (ESI[†]). These results indicate that the addition of butanol should be responsible for the preferred swelling of the hydrophobic volume of the block-copolymer micelles, leading first to the formation of micellar aggregates with decreased curvature (lamellar mesophase). Such a decrease in micelle curvature upon butanol addition was also observed previously for mesostructured silica obtained with cationic surfactant,⁹ or high concentrations of block copolymer.¹⁰ Evidently, silicates are loosely condensed at early stages of the formation of the lamellar mesophase. Upon further reaction at 35 °C or during hydrothermal treatment, condensation increases progressively in the silicate region, which possibly provokes folding and regular modulation of the silica surface inducing significant changes in micelle curvature. Thus, the lamellar mesophase is preferred at low degree of polymerization, and evolves into a highly ordered cubic *Ia3d* mesophase as the silica condensation proceeds further. Such phase transitions resulting from interplay between silica polymerization and organic packing constraints are well known under basic conditions for silica/cationic surfactant mesophases.^{11,12} However, no such phenomena have been demonstrated before for syntheses based on non-ionic triblock copolymers.

Mesoporous KIT-6 can be used for fabrication of carbon replicas with the same *Ia3d* symmetry, exhibiting either rod-type or tube-type structure depending on the synthesis conditions. Carbonization of sucrose leads to the rod-type carbon that is a faithful negative replica of the mesoporous *Ia3d* silica, as shown by XRD (Fig. 2a), with 3-D cubic arrangement of branched rods organized in two enantiomeric interwoven systems. The faithful replication without symmetry changes such as in the case of an MCM-48 template evokes the principle of CMK-3 synthesis,⁷ confirming the presence of porous bridges between the channel-like enantiomeric systems of the parent cubic silica. In contrast, the use of furfuryl alcohol under vacuum pyrolysis conditions produces the tube-type carbon (Fig. 2b), which consists of a cubic array of connected interpenetrating nanotubes or nanopipes. In that case, the entire pore volume is filled with furfuryl alcohol, and, after polymerization, tubes are subsequently generated in the middle of the

carbon framework, due to volume decrease occurring when the carbon source is heated under vacuum. In contrast to MCM-48, KIT-6 possesses pores that are large enough to allow the walls of the silica to be preferentially coated with a film of carbon, with the remaining carbon source being removed by evacuation. The XRD pattern of the tube-type carbon (example in Fig. 2b) is characterized by very low intensity of the (211) and (220) reflections, compared to the silica template or the rod-type carbon. The nitrogen adsorption isotherms of both carbons are type IV curves, giving high BET surface areas and pore volumes: 960 m² g⁻¹ and 0.70 cm³ g⁻¹ for rod-type, and up to 2200 m² g⁻¹ and 2.15 cm³ g⁻¹ for tube-type. The average pore size of the rod-type carbon is about 3 nm according to the BJH analysis, which reflects the wall thickness of the *Ia3d* silica template. The tube-type carbon exhibits a bimodal porosity with the inter-tube diameter (typically, 3 nm) and inner tube diameter (typically 5–6 nm).

In conclusion, this study has demonstrated a synthesis approach to high-quality large-mesoporous cubic *Ia3d* silicas, utilizing the phase-controlling (thermodynamic) effect of butanol in the SiO₂-EO₂₀PO₇₀EO₂₀-H₂O-HCl system, and also the micelle-folding (kinetic) effect during silicate polymerization. Increasing our insights into such thermodynamic and kinetic factors would be useful for synthesis of other mesostructured materials. Moreover, the present mesoporous silicas, obtained with tunable pore diameters between 4–12 nm, offer vast prospects for numerous future applications, due to their remarkably high surface areas and pore volumes, combined with highly accessible and highly connected open porous networks. This mesoporous silica would be useful as a template for nanofabrication of various materials such as other metal oxides, as well as the rod-type platinum, rod-type carbon and tube-type carbon as demonstrated here.

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Notes and references

[†] Sodium silicate (DC Chemical, Korea, 25 wt% aqueous solution, Si/Na = 1.5) was used with BuOH : P123 = 1.2 : 1 (wt%) and the reaction temperature was 25 °C before heating.

- X. Liu, B. Tian, C. Yu, F. Gao, S. Xie, B. Tu, R. Che, L.-M. Peng and D. Zhao, *Angew. Chem., Int. Ed.*, 2002, **41**, 3876.
- K. Flodström, V. Alfredsson and N. Källrot, *J. Am. Chem. Soc.*, 2003, **125**, 4402.
- Y.-T. Chan, H.-P. Lin, C.-Y. Mou and S.-T. Liu, *Chem. Commun.*, 2002, 2878.
- J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
- V. Alfredsson and M. W. Anderson, *Chem. Mater.*, 1996, **8**, 1141.
- H. J. Shin, R. Ryoo, Z. Liu and O. Terasaki, *J. Am. Chem. Soc.*, 2001, **123**, 1246.
- S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna and O. Terasaki, *J. Am. Chem. Soc.*, 2000, **122**, 10712.
- S. H. Joo, S. J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki and R. Ryoo, *Nature*, 2001, **412**, 169.
- P. Ågren, M. Lindén, J. B. Rosenholm, R. Schwarzenbacher, M. Krichbaum, H. Amenitsch, P. Lagner, J. Blanchard and F. Schüth, *J. Phys. Chem. B*, 1999, **103**, 5943.
- P. Feng, X. Bu and D. J. Pine, *Langmuir*, 2000, **16**, 5304.
- A. Monnier, F. Schüth, Q. S. Huo, D. Kumar, D. I. Margolese, R. S. Maxwell, G. D. Stucky, M. Krishnamurthy, P. Petroff, A. Firouzi, M. Janicke and B. F. Chmelka, *Science*, 1993, **261**, 1299.
- S. H. Tolbert, C. C. Landry, G. D. Stucky, B. F. Chmelka, P. Norby, J. C. Hanson and A. Monnier, *Chem. Mater.*, 2001, **13**, 2247.

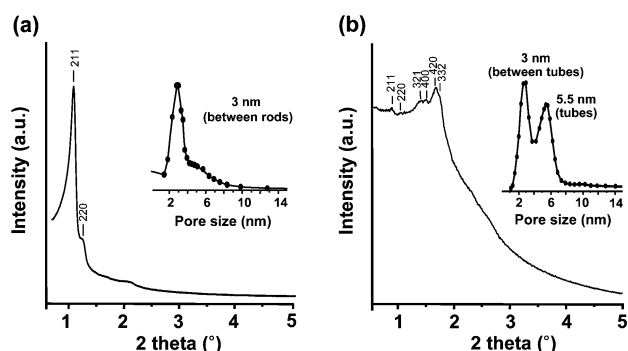


Fig. 2 XRD patterns for cubic *Ia3d* mesoporous carbons with (a) rod-type nanostructure ($a_{\text{CMK-8}} = 21.4$ nm), and (b) tubular nanostructure (from KIT-6 at 120 °C), with the respective pore size distributions obtained from N₂ physisorption at 77 K.